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In re Application of:

A. Nakajima et al.

Serial No. 10/647,169 .

Filed: August 21, 2003

For: INK-JET IMAGE FORMING

METHOD

DECLARATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Fumio ISHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 252360/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like

so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

Fumio ISHII

Dated: This 9th day of May, 2005.



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List of Documents Attached:

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SPECIFICATION

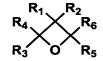
[TITLE OF THE INVENTION]

INK-JET IMAGE FORMING METHOD

WHAT IS CLAIMED IS:]

Claim 1. An actinic radiation curable resinous composition comprising a multifunctional oxetane compound having at least two oxetane rings in which at least one oxetane ring is an oxetane compound residual group represented by General Formula (1):

General Formula (1)



wherein R_1 - F_6 each represents a hydrogen atom, or a univalent or divalent organic group, and R_3 and R_4 or R_5 and R_6 do not simultaneously represent a hydrogen atom.

- Claim 2. An ink-jet ink comprising the aforesaid multifunctional oxetane compound and a photolytically acid generating compound.
- Claim 3. The ink-jet ink, described in claim 2, comprising a monofunctional oxetane compound.
- Claim 4. The ink-jet ink, described in claim 2, comprising either an epoxy compound or a vinyl ether compound.

Claim 5. An image forming method wherein the ink-jet ink described in any one of claims 2 - 4 is used, said ink is ejected onto a substrate surface, employing an ink-jet recording system, and said ink is cured while exposed to actinic radiation.

Claim 6. The image forming method, described in claim 5, wherein said actinic radiation is ultraviolet radiation.

[DETAILED DESCRIPTION OF THE INVENTION]
[0001]

[BACKGROUND OF THE INVENTION]

The present invention relates to an actinic radiation curable resinous composition and an ink-jet ink, as well as an image forming method using the same.

[0002]

[PRIOR ART]

With regard to oxetane compounds, production methods thereof as well as cation curable compositions comprised of the oxetane compounds, made have been various proposals.
[0003]

Japanese Patent Publication Open to Public Inspection
No. 2001-181386 discloses the 2-position substituted oxetane
compound and an actinic radiation curable composition using

the same. When the 2-position substituted oxetane compound is used in the actinic radiating curable composition, the resulting curability is relatively good. However, there are problems of the stability of oxetane compounds, the strength of cured layers and the close adhesion property to substrates.

[0004]

Japanese Patent Publication Open to Public Inspection
No. 2000-256571 proposes a thermocurable resinous composition
which employs a resin having a 2,4-position substituted
oxetane ring as a functional group. However, the practiced
compounds include only those having a 3-position substituted
oxetane ring and compounds having a 2,4-position substituted
oxetane ring are not specifically disclosed. Further, the
resinous composition is a thermally curable resinous
composition. The radiation energy curable composition as
described in the present invention is also not described.

Further, the compound described in the embodiment was incorporated into the actinic radiation curable composition of the present invention. As a result, the strength of the resulting layer was relatively good but there were problems

of the stability, curability and the close adhesion property to substrates.

[0006]

Japanese Patent Application Open to Public Inspection
Nos. 10-204072, 11-24654, 2000-86646, 2000-302774, and 200220376 disclose production methods of oxetane compounds
substituted at the 3-position, while Japanese Patent
Application Open to Public Inspection Nos. 8-143806, 11322735, and 2000-1482 disclose actinic radiation curable
compositions comprising compounds having 1 - 4 oxetane rings.
Disclosed compounds which have oxetane ring(s) are only those
which have the oxetane ring which is substituted at the 3position and do not describe the compounds of the present
invention. The stability of disclosed oxetane compounds is
relatively good. However, there are problems with
curability, strength of cured layers and close adhesion
property.

[0007]

Japanese Patent Application Open to Public Inspection Nos. 2001-220526 and 2002-188025 disclose actinic radiation curable ink-jet ink compositions comprising compounds having an oxetane ring substituted at the 3-position. In the same manner as above, the stability of the oxetane compounds is

relatively good. However, there are problems with the stability of the ink compositions, curability, the strength of cured layers and close adhesion property to substrates.

[0008]

Further, when low illuminance light sources, such as fluorescent lamps, are employed, cationically polymerizable oxetane compounds, which exhibit sufficient sensitivity under a high humidity ambience, are not currently available on the market.

[0009]

Still further, there is a problem with stable ejection from the ink-jet head.

[0010]

[PROBLEMS THEM PRESENT INVENTION INTENDS TO SOLVE]

Accordingly, an objective of the present invention is to provide a high speed actinic radiation curable resinous composition which exhibits excellent curability, strength of cured layers, and close adhesion property to substrate, and is independent of ambient humidity, as well as an ink-jet ink and an image forming method using the same.

[0011]

[MEANS TO SOLVE THE PROBLEMS]

An object of the present invention can be achieved by the following embodiments.

[0012]

1. An actinic radiation curable resinous composition comprising a multifunctional oxetane compound having at least two oxetane rings in which at least one oxetane ring is an oxetane compound residual group represented by General Formula (1):

General Formula (1)



wherein R_1 - F_6 each represents a hydrogen atom, or a univalent or divalent organic group, and R_3 and R_4 or R_5 and R_6 do not simultaneously represent a hydrogen atom.

2. An ink-jet ink comprising the aforesaid multifunctional oxetane compound and a photolytically acid generating compound.

[0014]

3. The ink-jet ink, described in item 2, comprising a monofunctional oxetane compound.

[0015]

- 4. The ink-jet ink, described in item 2, comprising either an epoxy compound or a vinyl ether compound.

 [0016]
- 5. An image forming method wherein the ink-jet ink described in any one of items 2 4 is used, said ink is ejected onto a substrate surface, employing an ink-jet recording system, and said ink is cured while exposed to actinic radiation.

[0017]

6. The image forming method, described in item 5, wherein said actinic radiation is ultraviolet radiation.

[0018]

(Oxetane Compounds)

Multifunctional oxetane compounds employed in the present invention will now be described.
[0019]

The multifunctional oxetane compounds in the present invention comprise at least two oxetane rings in which at least one of the oxetane rings is a residue of the oxetane compound substituted at the 2-position, represented by aforesaid General Formula (1). Preferred are compounds which comprises at least one of the residues of the oxetane compounds represented by aforesaid General Formula (1) in

which the 2-position is substituted, and further comprises an oxetane ring in which the 2-positin is not substituted. The residue of the oxetane compound, as described herein, refers to a univalent or higher valent group which is formed by extracting at least one hydrogen atom in the oxetane compound.

[0020]

In the oxetane compounds substituted at the 2-position, represented by aforesaid General Formula (1), R_1 - R_6 each represents a hydrogen atom or a univalent or divalent organic group, and R_3 and R_4 or R_5 and R_6 do not simultaneously represent a hydrogen atom.

[0021]

A multifunctional oxetane compound of the present invention, represented by aforesaid General Formula (1), has preferably a group derived from one of the oxetane ring represented by General Formulas (2) - (5) described below.

[0022]

General Formula (2)

$$\begin{array}{c|c}
R_1 & Z - R_7 \\
R_4 & R_6 \\
R_3 & O & R_5
\end{array}$$

General Formula (3)

$$\begin{array}{c|c}
R_1 & R_2 \\
R_4 & Z - R_7 \\
R_3 & O & R_5
\end{array}$$

General Formula (4)

$$R_8 - Z \xrightarrow{R_4} Z - R_7$$

General Formula (5)

$$R_8-Z \xrightarrow{R_1} R_2 Z-R_7$$

$$R_3 O R_5$$

[0023]

In General Formula (2) to (5), Z represents independently an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

 R_1 - R_6 each represents a hydrogen atom, a fluorine atom or an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), an fluorinated alkyl group having 1 - 6 carbon atoms, an ally group, an aryl group, a furyl group or a thienyl group.

 R_7 and R_8 each represents an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl

group or a butyl group), an alkenyl group having 1 - 6 carbon atoms (e.g., a 1-propenyl group, a 2-propenyl group, a 2-methyl-1-propenyl group, a 2-methyl-2-propenyl group, a 1-butenyl group, a 2-butenyl group, or a 3-butenyl group), an aryl group (e.g., a phenyl group, a benzyl group, a fluorobenzyl group, a methoxybenzyl group or a phenoxybenzyl group), an alkylcarbonyl group having 1 - 6 carbon atoms (e.g., a propylcarbonyl group, a butylcarbonyl group, or a pentylcarbonyl group), an alkoxycarbonyl group having 1- 6 carbon atoms (e.g., an ethoxycarbonyl group, a propoxycarbonyl group, or a butoxycarbonyl group), an alkylcarbamoyl group having 1 - 6 carbon atoms (e.g., a propylcarbamoyl group having 1 - 6 carbon atoms (e.g., a propylcarbamoyl group or a butylpentylcarbamoyl group, or an alkoxy carbamoyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbamoyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbamoyl group).

[0024]

In General Formulas (2) and (4), two pairs of R_3 and R_4 , as well as R_5 and R_6 do not represent a hydrogen atom at the same time.

[0025]

Of the aforesaid substituents, R_1 is preferably a lower alkyl group, specifically, an ethyl group is preferably employed. Further, R_7 and R_8 is preferably a propyl group, a

butyl group, a phenyl group, or a benzyl group. Z is preferably a hydrocarbon group having neither an oxygen atom nor a sulfur atom.

[0026]

A preferable multifunctional oxetane compound having an oxetane group substituted at position 2 is as follows. The multifunctional oxetane compound may contain two or more oxetane groups substituted at position 2, or may further contain a oxetane group non-substituted at position 2.

[0027]

Further, in the present invention, it is possible to employ a multifunctional oxetane compound having at least two oxetane rings in the molecule, which are represented by General Formulas (6) and (7) described below.

[0028]

General Formula (6)

$$\begin{bmatrix} R_1 & Z \\ R_4 & R_6 \\ R_3 & 0 & R_5 \end{bmatrix}_m$$

General Formula (7)

$$\begin{bmatrix} R_1 & R_2 \\ R_4 & C \\ R_3 & C \\ R_5 \end{bmatrix}_m R_9$$

[0029]

In General Formulas (6) and (7); m represents 2, 3, or 4; Z represents independently an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

 R_1 - R_6 each represents a hydrogen atom, a fluorine atom or an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), an fluorinated alkyl group having 1 - 6 carbon atoms, an ally group, an aryl group, a furyl group. [0030]

R₉ represents a straight or branched alkylene group having 1 - 12 carbon atoms. Examples are alkylene groups represented by General Formula (8) described below.
[0031]

General Formula (8)

[0032]

wherein R_{10} represents a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group).

In General Formula (6) and (7), R_9 represents a polyvalent group represented by General Formulas (9),(10) and (11).

[0033]

General Formula (9)

[0034]

In General Formula (9), n represents 0 or an integer of 1-2,000, R_{11} represents an alkyl group having 1-10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group), or the group represented by General Formula (12) described below.

 R_{12} represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group).

[0035]

General Formula (12)

[0036]

In General Formula (12), j represents 0 or an integer of 1 - 100, and R_{13} represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group).

[0037]

General Formula (10)

[8800]

In General Formula (10), R₁₄ represents a hydrogen atom or an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group and a butyl group), an alkoxy group having 1 - 10 carbon atoms (e.g. a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and a pentoxy group), a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), a nitro group, a cyano group, a mercapto group, an alkoxycarbonyl group of low alkyl number (e.g., a methyloxycarbonyl group, an ethyloxycarbonyl group, or a butyloxycarbonyl group), or a carboxyl group.

[0039]

General Formula (11)

[0040]

In General Formula (11), R_{15} represents an oxygen atom, a sulfur atom, -NH-, -SO-, -SO₂-, -CH₂-, -C(CH₃)₂-, or -C(CF₃)₂-.

[0041]

Embodiments of the preferred partial structure of compounds having an oxetane ring employed in the present invention are as follows. For example, in aforesaid General Formulas (6) and (7), R_1 is preferably a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group), and is more preferably an ethyl group. Further, preferably employed as R_9 is a hexamethylene group or a group in which R_{14} is a hydrogen atom in aforesaid General Formula (10). Z is a hydrocarbon group which contains neither an oxygen atom nor a sulfur atom.

[0042]

Further, listed as one example of preferred embodiments of compounds having an oxetane ring according to the present invention is the compound represented by General Formula (13) described below.

[0043]

General Formula (13)

[0044]

In General Formula (13), r represents an integer of 25 – 200; R_{16} represents an alkyl group having 1 – 4 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, or a butyl group), or a trialkylsilyl group; R_1 and R_3 indicate the same group as above.

Two pairs of R_3 and R_4 as well as R_5 and R_6 do not represent a hydrogen atom at the same time. [0045]

In multifunctional oxetane compounds in the present invention, all the oxetane rings may be substituted at the 2-position or the 4-position as represented by General Formula (1), or the oxetane ring represented by General Formula (1) as well as the oxetane ring which is not substituted at the 2-position or the 4-position may be included. Further, it is

preferable that 1-15 oxetane rings are incorporated in the aforesaid compound and that the average molecular weight thereof is 50-2,000.

[0046]

Of these, in the present invention, preferably employed are multifunctional oxetane compounds which comprise oxetane ring(s) which are substituted at the 2-position as a partial structure in the form of the residue of the oxetane compound, together with the oxetane ring structure in which the 2-position is not substituted.

[0047]

Specific examples of compounds having a plurality of oxetane rings are as follows.

[0048]

1
$$H_3CO$$
2 H_3CO
3 O
4 O
5 O
6 O
7 O
1 O
1 O
2 O
3 O
6 O
7 O
1 O
1 O
1 O
2 O
3 O
4 O
4 O
6 O
7 O
1 O
1

It is possible to synthesize the compounds according to the present invention, which have an oxetane ring being substituted at least position 2, with reference to publications described below.

[0050]

[0049]

(1) Hu Xianming, Richard M. Kellogg, Synthesis, 533 - 538,

May (1995)

- (2) A. O. Fitton, J. Hill, D. Ejane, R. Miller, Synth., 12, 1140 (1987)
- (3) Toshiro Imai and Shinya Nishida, Can. J. Chem. Vol. 59, 2503 2509 (1981)
- (4) Nobujiro Shimizu, Shintaro Yamaoka, and Yuho Tsuno, Bull.

 Chem. Soc. Jpn., 56, 3853 3854 (1983)
- (5) Walter Fisher and Cyril A. Grob, Helv. Chim. Acta., 61, 2336 (1987)
- (6) Chem. Ber. 101, 1850 (1968)
- (7) "Heterocyclic Compounds with Three- and Four-membered Rings", Part Two, Chapter IX, Interscience Publishers, John Wiley & Sons, New York (1964)
- (8) Bull. Chem. Soc. Jpn., 61, 1653 (1988)
- (9) Pure Appl. Chem., A29 (10), 915 (1992)
- (10) Pure Appl. Chem., A30 (2 & amp; 3), 189 (1993)
- (11) Japanese Patent Application Open to Public Inspection
 No. 6-16804
- (12) DE 10221858

The amount of compounds according to the present invention, which have an oxetane ring in which at least position 2 is substituted, in a photocurable ink is

preferably 1 - 97 percent by weight, and is more preferably 30 - 95 percent by weight.

[0051]

By employing these compounds according to the present invention together with oxetane compounds which are not substituted at the 2-position, it is possible to result in dramatically enhanced effects in reaction rate, and to realize an adequate curing rate even under high humidity ambience.

[0052]

Employed as oxetane compounds which are not substituted at the 2-position may be those, known in the art, which are introduced in Japanese Patent Application Open to Public Inspection Nos. 2001-220526 and 2001-310937.

Of compounds having oxetane ring(s), preferred are those which have 1-4 oxetane rings.

It is preferable that compounds, according to the present invention having oxetane ring(s), in which at least the 2-position is substituted, are simultaneously employed. Specific examples of oxetane compounds will now be described. [0055]

The compounds having an oxetane ring in the molecule are represented by the following General Formula (1). [0056]

General Formula (1)

$$R^1$$
 O R^2

[0057]

In the General Formula (1), R¹ is a hydrogen atom, alkyl group having 1 - 6 carbon atoms such methyl group, ethyl group, propyl group or butyl group, fluoro-alkyl group having 1 to 6 carbon atoms, allyl group, aryl group, furyl group, or thienyl group. R² is an alkyl group having 1 to 6 carbon atoms such as methyl group, ethyl group, propyl group or butyl group; alkenyl group having 2 to 6 carbon atoms such as 1-propenyl group, 2-propenyl group, 2-methyl-1-propenyl group, 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group or 3-butenyl group; a group having aromatic ring such as phenyl group, benzyl group, fluoro-benzyl group, methoxybenzyl group or phenoxy-ethyl group; alkyl carbonyl group having 2 to 6 carbon atoms such as ethyl carbonyl group, propyl carbonyl group or butyl carbonyl group; alkoxy carbonyl group having 2 to 6 carbon atoms such as ethoxy

carbonyl group, propoxy carbonyl group or butoxy carbonyl group; N-alkyl carbamoyl group having 2 to 6 carbon atoms such as ethyl carbamoyl group, propyl carbamoyl group, butyl carbamoyl group or pentyl carbamoyl group. As the oxetane compound used in the present invention, it is particularly preferable that the compound having one oxetane ring is used, because the obtained composition is excellent in the coking property, and the operability is excellent in the low viscosity.

[0058]

The compounds having two oxetane rings in the molecule are represented by the following General Formula (2).
[0059]

General Formula (2)

$$R^1 \longrightarrow R^3 \longrightarrow R^2$$

[0060]

In the General Formula (2), R¹ is the same group as the group shown in the above-described General Formula (1). R³ is, for example, a linear or branching alkylene group such as ethylene group, propylene group or butylene group; linear or branching poly (alkylene-oxy) group such as poly (ethylene

oxy) group or poly (propylene oxy) group; linear or branching un-saturated hydrocarbon group such as propenylene group, methyl propenylene group or butenylene group; carbonyl group; alkylene group including carbonyl group; alkylene group including carboxyl group; alkylene group including carboxyl group; alkylene group including carbamoyl group.

[0061]

Further, R^3 may also be a polyhydric group selected from the group shown by the following General Formulas (3), (4) and (5).

[0062]

General Formula (3)

[0063]

In the General Formula (3), R⁴ is a hydrogen atom, an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or alkoxy group having 1 to 4 carbon atoms such as methoxy group, ethoxy group, propoxy group or butoxy group, or halogen atom such as chloride atom or bromine atom, nitro group, cyano group, mercapto group, lower alkyl carboxyl group such as the group

having 1 to 5 carbon atoms, carboxyl group, or carbamoyl group.

[0064]

General Formula (4)

[0065]

In the General Formula (4), R^5 is oxygen atom, sulfide atom, methylene group, -NH-, -SO-, -SO₂-, -C(CF₃)₂-, or -C(CH₃)₂-.

[0066]

General Formula (5)

[0067]

In the General Formula (5), R^6 is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or aryl group. Numeral n is an integer of 0 - 2000. R^7 is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or aryl group. R^7 is also a group selected from the group shown by the following General Formula (6).

[8800]

General Formula (6)

$$-O - \left(\begin{matrix} R^8 & R^8 \\ I & I \\ Si - O \end{matrix}\right)_{m} \begin{matrix} Si - R^8 \\ I \\ R^8 & R^8 \end{matrix}$$

[0069]

In the General Formula (6), R^8 is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or aryl group. Numeral m is an integer of 0 - 100.

[0070]

As a specific example of the compound having 2 oxetane rings, the compounds shown by the following structural formulas are listed.

[0071]

Exemplified compound 1

Exemplified compound 2

[0072]

Exemplified compound 1 shown by the above structural formula is a compound in which R^1 is an ethyl group, and R^3 is a carboxy group in General Formula (2).

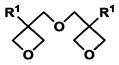
Exemplified compound 2 shown by the above structural formula is a compound in which each R^6 and R^7 are a methyl group, and n is 1 General Formula (5).

[0073]

Among the compound having 2 oxetane rings, as a preferable example except for the above-described compounds, there are compounds shown by the following General Formula (7). In the General Formula (7), R¹ is the same group as in the General Formula (1).

[0074]

General Formula (7)



[0075]

As the compounds having 3-4 oxetane rings, the compounds shown in the following General Formula (8) are listed.

[0076]

General Formula (8)

$$\begin{bmatrix} R^1 & O \\ O & J \end{bmatrix}$$

[0077]

In the General Formula (8), R¹ is the same group as in the General formula (1). R⁹ is, for example, branching alkylene group having 1 to 12 carbon atoms such as groups shown by the following General Formulas (9), (10), branching poly(alkylene oxy) group such as group shown by the following General Formula (11), or branching polysiloxane group such as group shown by the following General Formula (12) is listed. Numeral j is 3 or 4.

[0078]

Α

В

С

$$-\mathsf{CH_2} - \mathsf{CH_2} - \mathsf{CH} - \mathsf{CH_2} - \mathsf{CH} - \mathsf{CH_2} - \mathsf{CH_2} -$$

D

$$\begin{array}{c} \text{CH}_{2} - \left(\text{OCH}_{2} \text{CH}_{2} \right)_{p} \\ - \left(\text{CH}_{2} \text{CH}_{2} \text{O} \right)_{p} \text{CH}_{2} - \left(\text{CH}_{2} \text{CH}_{3} \right) \\ \text{CH}_{2} - \left(\text{OCH}_{2} \text{CH}_{2} \right)_{p} \end{array}$$

Ε

[0079]

In Formula A, R^{10} is a lower alkyl group such as a methyl, ethyl, or propyl group. In Formula D, p is an integer of 1 to 10.

[0080]

As the specific example of the compound having 3 to 4 oxetane rings, the compound shown in the following Exemplified compound 3 is cited.

[0081]

Exemplified compound 3

[0082]

Furthermore, as an example of the compounds having 1 - 4 oxetane rings except the above examples, there are compounds shown in the following General Formula (9).

[0083]

General Formula (9)

[0084]

In the General Formula (9), R^1 is the same group as in General Formula (1) and R^8 is the same group as in the General Formula (6). R^{11} is alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or tri-alkyl silyl group, and r is an integer of 1-4.

[0085]

As preferable specific examples of the oxetane compounds used in the present invention, are compounds 4, 5, and 6 shown below.

[0086]

Exemplified compound 4

Exemplified compound 5

$$\bigcirc \bigcirc$$

Exemplified compound 6

[0087]

The preparation method of the compounds having the oxetane ring is not particularly limited, and it may be conducted according to the conventionally known method as as described in the references cited above. One of the examples is a synthetic method of an oxetane ring from diol disclosed by Pattison (D. B. Pattison, J. Am. Chem. Soc., 3455, 79 (1957)).

Further, other than them, compounds having 1 - 4 oxetane rings, which have high molecular weight of molecular weight of about 1000 - 5000, are also listed. As an example of them, for example, the following compounds 7, 8 and 9 are listed.

[0088]

Exemplified compound 7

Exemplified compound 8

Exemplified compound 9

s:20~200

[0089]

Further, the aforesaid compound having an oxetane ring substituted at position 2 may be employed in combination with photopolymerizable compounds. Such photopolymerizable monomers are cationic polymerizable monomers. Listed examples of the monomers are epoxy compounds, vinyl ether compounds.

[0090]

As epoxy compounds, the following aromatic epoxides, alicyclic epoxides and aliphatic epoxides can be used.
[0091]

As preferable aromatic epoxides are listed, di- or poly-glycidyl ether, which is synthesized by the reaction of polyhydric phenol having at least one aromatic core or alkylene oxide-added polyhydric phenol and epichlorohydrin, and for example, di- or poly-glycidyl ether of bisphenol A or of alkylene oxide-added bisphenol A, di- or poly-glycidyl ether of hydrogenated bisphenol A or of alkylene oxide-added hydrogenated bisphenol A, and novolak type epoxy resin. Herein, as alkylene oxide, ethylene oxide and propylene oxide are listed.

[0092]

As preferable alicyclic epoxides are listed, a cyclohexene oxide or cyclopentene oxide, which is obtained by epoxidation of the compound having cycloalkane ring such as at least one cyclohexene or cyclopentene ring by the appropriate oxidant such as hydrogen peroxide or peracid.

[0093]

As preferable aliphatic epoxides are listed, di- or poly-glycidyl ether of aliphatic polyvalent alcohol or of alkylene oxide-added aliphatic polyvalent alcohol, and as its representative example, di-glycidyl ether of alkylene glycol such as di-glycidyl ether of ethylene glycol, di-glycidyl ether of propylene glycol and glycidyl ether of 1, 6-hexane

diol, poly-glycidyl ether of polyvalent alcohol such as di-or tri-glycidyl ether of glycerin or of alkylene oxide added glycerin, and di-glycidyl ether of polyalkylene glycol such as di-glycidyl ether of polyethylene glycol or of alkylene oxide-added polyethylene glycol, and di-glycidyl ether of polypropylene glycol or of alkylene oxide-added polypropylene glycol, are listed. Herein, as alkylene oxide, ethylene oxide and propylene oxide.

Among these epoxides, when the quick hardening ability is considered, aromatic epoxide and alicyclic epoxide are preferable, and particularly, alicyclic epoxide is preferable. In the present invention, on kind of the above epoxides may be solely used, and more than 2 kinds of them may also be used by appropriately being combined.

[0095]

[0094]

Also as vinyl ether compounds preferably used in the ink of the present invention are listed: publicly known vinyl ether compounds can be used, and for example, di or tri-vinyl ether compound, such as ethylene glycol di-vinyl ether, di-ethylene glycol di-vinyl ether, tri-ethylene glycol di-vinyl ether, propylene glycol di-vinyl ether, di-propylene glycol di-vinyl ether, butane diol di-vinyl ether, hexane diol di-

vinyl ether, cyclohexane di-methanol di-vinyl ether, trimethylol propane tri-vinyl ether, or mono vinyl ether
compound, such as ethyl vinyl ether, n-butyl vinyl ether,
iso-butyl vinyl ether, octadecyl vinyl ether, cyclohexyl
vinyl ether, hydroxy butyl vinyl ether, 2- ethyl-hexyl vinyl
ether, cyclo-hexane di-methanol mono-vinyl ether, n-propyl
vinyl ether, iso-propyl vinyl ether, iso-propenyl ether-opropylene carbonate, dodecyl vinyl ether, or di-ethylene
glycol mono vinyl ether vinyl ether.
[0096]

Among these vinyl ether compounds, when the hardenability, adhesion or surface hardness is considered, di or tri-vinyl ether compound is preferable, and particularly di-vinyl ether compound is preferable. In the present invention, one kind of the above vinyl ether compounds may also be used, and more than two kinds of them may also be used by being appropriately combined.

[0097]

As photo initiators, all publicly known photo acid generators (a compound which generates the acid by the active ray, such as ultraviolet rays) can be used. As the photo acid generator, for example, a chemical amplification type photo resist or compound used for the light cationic

polymerization is used (Organic electronics material seminar "Organic material for imaging" from Bunshin publishing house (1993), refer to page 187 - 192). Examples preferable for the present invention will be listed below.

Firstly, aromatic onium compound $B(C_6F_5)_4$, PF_6 , AsF_6 , SbF_6 , CF_3SO_3 salt, such as diazonium, ammonium, iodonium, sulfonium, phosphonium, can be listed. [0099]

Specific examples of the onium compounds will be shown below.

[0100]

[0101]

Secondly, sulfone compounds, which generate sulfonic acid, can be listed. Examples of specific compounds will be shown below.

[0102]

[0103]

Thirdly, halogenide which generates hydrogen halide can also be used. Examples of specific compounds will be shown below.

[0104]

$$CI \longrightarrow \begin{matrix} CCI_3 \\ CH \longrightarrow \end{matrix} \longrightarrow CI \qquad CH_3O \longrightarrow CH_2CI \qquad CH_2CI \qquad CH_3O \longrightarrow CH_2CI \qquad CCI_3$$

$$O \longrightarrow \begin{matrix} CH_3 \\ CCI_3 \end{matrix} \longrightarrow HO \longrightarrow HICOOCH_2CCI_3 \quad CH_3O \longrightarrow HO$$

[0105]

Fourthly, ferrite allene complex can be listed. [0106]

[0107]

Further, the actinic radiation curable composition of the present invention is cured by exposure to actinic radiation such as ultraviolet radiation. In order to more efficiently conduct such curing reaction, it is possible to simultaneously use photosensitizers. Examples of such photosensitizers include amines such as triethanolamine, methyldiethanolamine, triisopropanolamine, methyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, ethyl 2-diethylaminobenzoate, n-butoxyethyl 4-dimethylaminobenzoate, and 2-ethylhexyl 4-dimethylaminobenzoate, cyanine, phthalocyanine, merocyanine, porphyrin, spiro compounds, ferrocene, fluorene, flugide, imidazole, perylene, phenazine, phenothiazine, polyene, azo compounds, diphenylmethane, triphenylmethane, polymethine acridine, coumarin, ketocoumarin, quinacridone, indigo,

styryl, pyrylium compounds, pyrromethene compounds, pyrazolotriazole compounds, benzothiazole compounds, barbituric acid derivatives, and thiobarbituric acid derivatives. Further, employed are compounds described in European Patent No. 568,993, U.S. Patent Nos. 4,508,811 and 5,227,227, and Japanese Patent Application Open to Public Inspection Nos. 2001-125255 and 11-271969. The used amount of photosensitizers is preferably in the range of 0.01 - 10.00 percent by weight in the actinic radiation curable composition.

[0108]

In order to color an active ray curable resin composition or an ink-jet ink of the present invention, colorants may be added thereto.

As the colorants in the present invention are, the colorants, which can be solved or dispersed in main component of the polymeric compound, can be used, however, from the viewpoint of weather fastness, the pigment is preferable.

[0110]

As the pigment, the followings can be used.

C.I. Pigment Yellow-1, 3, 12, 13, 14, 17, 81, 83, 87, 95, 109, 42,

- C. I. Pigment Orange-16, 36, 38,
- C. I. Pigment Red-5, 22, 38, 48:1, 48:2, 48:4, 49:1, 53:1,
- 57:1, 63:1, 144, 146, 185, 101,
- C. I. Pigment Violet-19, 23,
- C. I. Pigment Blue-15:1, 15:3, 15:4, 18, 60, 27, 29,
- C. I. Pigment Green-7, 36
- C. I. Pigment White-6, 18, 21,
- C. I. Pigment Black-7.

Further, in the present invention, in order to enhance covering power of color on transparent substrates such as plastic film, it is preferable to use a white ink.

Specifically, in soft package printing and label printing, it is preferable to use a white ink. However, since the ejection amount increases, from the viewpoint of the aforesaid ejection stability, and the formation of curling and wrinkling, the amount to be used is obviously limited.

[0111]

To disperse the pigment, a ball mill, sand mill, attritor, roll mill, agitator, Henschel mixer, colloid mill, ultrasonic homogenizer, Pearl mill, wet jet mill, or paint shaker may be used. Further, when the pigment is dispersed, the dispersing agent can also be added. It is preferable that, as the dispersing agent, high polymeric dispersing

agent is used. As the high polymeric dispersing agent, Solsperse series of Avecia co., is cited.

Further, as the dispersion auxiliary agent, the synergist corresponding to each kind of pigment can also be used. It is preferable that 1 - 50 parts by weight of these dispersing agent and dispersion auxiliary agent are added to 100 parts by weight of the pigment. The dispersion medium is solvent or polymeric compound, and it is preferable that the ultraviolet ray-curable ink used in the present invention comprises no-solvent, because it is reacted and hardened just after the arrival of the ink. When the solvent remains in the hardened image, the problem of deterioration of solvent resistance and VOC (Volatile Organic Compound) of the remained solvent is raised. Accordingly, it is preferable in the dispersion aptitude that the dispersion medium is not solvent, but polymeric compounds, and the monomer in which the viscosity is lowest in them, is selected.

[0112]

When the dispersion is conducted, it is preferable to configure the pigment, dispersing agent, selection of diluent for the dispersion so that average particle size of the pigment become 0.08 - 0.5 μm , more preferably 0.3 - 10 μm ,

still more preferably, $0.3-3~\mu m$. By this particle size control, the nozzle plugging of the ink-jet head is suppressed, and the preservation stability of the ink, ink transparency and hardening sensitivity can be maintained. [0113]

It is preferable for the colorant that the addition amount is 1 weight% to 10 weight% of the whole of the ink. [0114]

To disperse the pigment, a ball mill, sand mill, attritor, roll mill, agitator, Henschel mixer, colloid mill, ultrasonic homogenizer, Pearl mill, wet jet mill, or paint shaker may be used. Further, when the pigment is dispersed, the dispersing agent can also be added.

[0115]

It is preferable that, as the dispersing agent, high polymeric dispersing agent is used. As the high polymeric dispersing agent, Solsperse series of Avecia co., is cited.

Further, as the dispersion auxiliary agent, the synergist corresponding to each kind of pigment can also be used. It is preferable that 1 - 50 parts by weight of these dispersing agent and dispersion auxiliary agent are added to 100 parts by weight of the pigment.

[0116]

Employed as dispersion media are solvents or polymerizable compounds. The actinic radiation curable ink is preferably free from solvents to undergo reaction and curing after ink impingement. When the aforesaid solvents remain in cured images, problems occur with degradation of solvent resistance as well as VOC (volatile organic compound) of residual solvents. Therefore, from the viewpoint of dispersion adaptability, it is preferable to use as the dispersion media, polymerizable compounds instead of solvents [0117]

When the dispersion is conducted, it is preferable to configure the pigment, dispersing agent, selection of diluent for the dispersion so that average particle size of the pigment become $0.08-0.5~\mu m$, more preferably $0.3-10~\mu m$, still more preferably, $0.3-3~\mu m$. By this particle size control, the nozzle plugging of the ink-jet head is suppressed, and the preservation stability of the ink, ink transparency and hardening sensitivity can be maintained.

When the dispersion is conducted, it is preferable to configure the pigment, dispersing agent, selection of diluent for the dispersion so that average particle size of the pigment become 0.08 - 0.5 μ m, more preferably 0.3 - 10 μ m,

still more preferably, 0.3 - 3 μ m. By this particle size control, the nozzle plugging of the ink-jet head is suppressed, and the preservation stability of the ink, ink transparency and hardening sensitivity can be maintained. [0118]

Other than the compounds described above, it is possible to use various additives in the actinic radiation curable composition according to the present invention. For example, in order to enhance the storage stability of compositions, it is possible to add polymerization inhibitors in an amount of 2,000 - 20,000 ppm. It is preferable that an ultraviolet radiation curable ink is ejected while heated to decrease its viscosity. As a result, in order to minimize clogging of head nozzles due to thermal polymerization, it is preferable to add polymerization inhibitors. Other than these, if desired, it is possible to add surface active agents, leveling additives, matting agents, polyester based resins, polyurethane resins, vinyl based resins, acryl based resins, rubber based resins, and wax to adjust physical properties of layers. In order to improve close adhesion properties to recording media, it is effective to add organic solvents in very minute amounts. In such cases, the aforesaid addition is effective in a range in which solvent

resistance is not adversely affected and negligible VOC problems occur. The used amount is in the range of 0.1-5 percent and preferably in the range of 0.1-3 percent. [0119]

Further, incorporated as additives to actinic radiation curable resinous compositions in the present invention may be reaction retarding agents, fillers, fluid aids, thixotropy agents, humectants, defoamers, and plasticizers. Further added may be stabilizers such as lightfastness enhancing agents, UV absorbers, antioxidants, polymerization inhibitors or corrosion inhibitors, or Si based compounds and wax. In order to adjust surface tension, if desired, incorporated may be surface active agents.

[0120]

In order to control surface tension, if desired, surface active agents may be incorporated. Examples of surface active agents, which are preferably employed in the present invention, include anionic surface active agents such as dialkylsulfosuccinic acid salts, alkylnaphthalenesulfonic acid salts, and fatty acid salts; nonionic surface active agents such as polyoxyethylene alkyl allyl ethers, acetylene glycols, and polyoxyethylene-polyoxypropylene block polymers; and cationic surface active agents such as alkylamine salts

and quaternary ammonium salts. Of these, specifically preferred are anionic surface active agents as well as nonionic surface active agents.

[0121]

An image forming method, employing the actinic radiation curable resinous composition according to the present invention, will now be described.

[0122]

A method which is preferred as the image forming method of the present invention is that the aforesaid actinic radiation curable resinous composition is ejected as an ink composition onto a recording material, employing an ink-jet recording system to form images, and subsequently the ink is cured while exposed to actinic radiation such as ultraviolet radiation.

[0123]

In the present invention, the total ink layer thickness after curing, while ink comprised of the actinic radiation curable resinous composition according to the present invention, is impinged on the recording material and exposed to actinic radiation is preferably 2 - 20 μ m. In the actinic radiation curable ink-jet recording of the screen printing field, at present, the total ink layer thickness usually

exceeds 20 µm. In the soft package printing field, in which recording materials are comprised of relatively thin plastic materials, excessive ink ejection, which results in a thick ink layer, is not preferred because problems occur in which stiffness as well as the feeling of quality of the entire printed materials varies, in addition to the aforesaid problems of curling and wrinkling of recording materials.

Incidentally, "total ink layer thickness", as described herein, refers to the maximum value of the ink layer thickness of images formed on recording materials. The aforesaid total layer thickness is applied in the same manner, even though 2-color overprinting (secondary color), 3-color overprinting, or 4-color overprinting (a white ink base) is carried out employing ink-jet recording systems.

[0125]

Preferred ink ejection conditions are such that the recording head and the ink are heated to $35-100\,^{\circ}\text{C}$ and preferably to $35-80\,^{\circ}\text{C}$ to result in stable ejection.

The viscosity of an actinic radiation curable ink
varies widely depending on temperature variation. The
resulting viscosity variation results in major effects to the

liquid droplet size as well as the liquid droplet ejection rate to degrade image quality. As a result, it is necessary to maintain the raised temperature at a constant value. The controlled temperature range of ink temperature is preferably set temperature ±5 °C, more preferably set temperature ±2 °C, and still more preferably set temperature ±1 °C.

Further, in the present invention, the volume of liquid droplets ejected from each nozzle is preferably 2 - 15 pl. [0127]

Originally, in order to form highly detailed images, it is necessary to maintain the volume of liquid droplets in the aforesaid range. However, when the aforesaid volume of a single liquid droplet is ejected, it becomes more difficult to achieve the aforesaid ejection stability. According to the present invention, even though ejection is carried out at a small droplet volume such as 2 - 15 pl, ejection stability is enhanced, whereby it is possible to consistently form highly detailed images.

[0128]

In the present invention, actinic radiation sources which are used as an exposure means include those which emit

near infrared radiation, visible light, ultraviolet radiation, or electron beams. Of these, preferred are radiation sources which emit the radiation in the ultraviolet wavelength region and more preferred are radiation sources which emit radiation having a dominant wavelength of 300 - 400 nm. Examples include low pressure mercury lamps, high pressure mercury lamps, metal halide lamps, excimer lamps, xenon lamps, halogen lamps, fluorescent lamps, cold cathode tubes, electrode-free UV lamps, lasers, and LEDs.

In the present invention, radiation means includes exposure of actinic radiation onto a substrate from a radiation source. For example, Japanese Patent Publication Open to Public Inspection No. 60-132767 discloses a method in which an ultraviolet radiation lamp is moved together with a recording head which scans above recording media, and U.S. Patent No. 6,145.979 discloses a method in which ultraviolet radiation is introduced to the side of a recording head from an ultraviolet radiation source arranged in a position separate from the recording head, employing an optical system such as optical fibers, collimators, or mirrors. Further, as shown in Japanese Patent Application No. 2001-350219, it is possible to arrange a linear radiation source crossing from

the upper section of a recording head across the width. Incidentally, illuminance, as described in the present invention refers to the total exposure energy of the actinic radiation, while exposure timing, as described herein, means the time to initiate exposure after ink impingement. Peak wavelength, as described herein, refers to the wavelength having maximum exposure energy of actinic radiation having a wavelength of at most 450 nm, while peak illuminance refers to the illuminance at the peak wavelength. Further, exposure time refers to the time in which, in the exposure section, actinic radiation having at least 1/10 of the maximum illuminance is exposed. In the present invention, spectral illuminance is determined employing a Spectrophotometer USR-40D, manufactured by Ushio Denki Co., while setting the measurement pitch at 10 nm.

[0130]

Other exposure means usable in the present invention include aforesaid exposure means applying methods in which actinic radiation can be exposed to substrates. Examples include a method in which by utilizing the method moving the ultraviolet radiation lamp together with the recording head, the radiation source is placed on a carriage, and actinic radiation is exposed while operating recording media, and a

method in which ultraviolet radiation is introduced to the side of a recording head, employing optical systems such as optical fibers, collimators, and mirrors. Further, it is possible to arrange a linear radiation source which gives exposure onto the entire portion of substrate across the width. In the exposure means according to the present invention, it is possible to achieve exposure while dividing radiation emitted from one source employing a first and a second exposure means such as filters or mirrors.

In the present invention, it is preferable that actinic radiation is exposed 0.001 - 1 second after impingement of the actinic radiation curable ink. When the exposure interval of exposure radiation is at most 0.001 second, the distance between nozzles and the radiation source becomes too narrow, whereby the head may be stained with sublimed materials formed by curing or nozzles may be clogged due to stray light. On the other hand, when it is at least 1 second, the effects of the present invention are not fully exhibited.

[0132]

Specifically it is preferable that radiation exposure starts 0.01 - 2 seconds, preferably 0.01 - 0.4 second after

impingement of the ink on the substrate and radiation exposure is terminated after 0.1 - 3 seconds, preferably after 0.2 - 1 second so that ink fluidity almost disappears. By doing so, it is possible to minimize an increase in the dot size as well as bleeding of dots.

[0133]

Further, in the present invention, one of the preferred embodiments of the exposure method of actinic radiation is that the actinic radiation has a peak illuminance of 1-500 mW/cm² as the effective curing wavelength.

Still further, in the present invention, another preferred embodiment of the exposure method of actinic radiation is that the peak illuminance of the actinic radiation in the effective wavelength region for curing is $500 - 2,000 \, \text{mW/cm}^2$.

[0135]

Printed matter employing the actinic radiation curable resinous composition (ink) of the present invention will now be described.

[0136]

Printed matter of the present invention is characterized in being prepared by employing the image

forming method of the present invention, and/or the image forming apparatus described in the present invention, while using non-absorptive recording materials. "Non-absorptive", as described herein, means that the actinic radiation curable resinous composition (ink) is not absorbed. In the present invention, recording materials which have an ink transfer amount of at most 0.1 ml/mm² determined by Bristow's method, described below, or substantially 0 ml/mm² are defined as non-absorptive recording materials.

[0137]

Bristow's method, as described in the present invention, refers to the method which determines liquid absorption behavior of paper and paper board over a short time period. In practice, measurement is performed in accordance with J. TAPPI Paper and Pulp Test Method No. 51-87 Test Method of Liquid Absorption of Paper or Paper Board (Bristow's Method). The resulting liquid absorption is represented by ink transfer amount (ml/m²) within a contact time of 40 milliseconds. Incidentally, in the aforesaid measurement method, pure water (such as ion exchanged water) is employed. However, in the present invention, in order to easily discriminate already measured areas, water-soluble dyes may be incorporated in an amount of at most 2 percent.

[0138]

One example of the specific measurement methods will now be described.

The ink transfer amount is measured as follows. A recording medium is allowed to stand at an ambience of 25 °C and 50 percent relative humidity for at least 12 hours.

Thereafter, measurement is carried out employing Bristow

Tester Type II (a pressing system), manufactured by Kumagai

Riki Kogyo Co., Ltd., which is a dynamic liquid absorbability testing device. In order to enhance measurement accuracy, a commercially available water based ink-jet ink (e.g., magenta ink) is employed as the liquid used for the measurement.

After the specified contact time, it is possible to determine the ink transfer amount by measuring the magenta dyed area on the recording medium.

[0139]

As supports for the present invention, various types of non-absorptive supports can be used other than common coated paper and non-coated paper. Among them, preferably used are non-absorptive plastics and film supports used for soft packaging materials.

Examples of non-absorptive supports are various types of plastic films including PET (polyethylene terephthalate)

film, OPS (oriented polystyrene) film, OPP (oriented polypropylene) film, ONy (oriented nylon) film, PVC (polyvinyl chloride) film, PE film, and TAC film. Employed as other plastic films may be polycarbonate, acrylic resins, ABS, acetal, PVA, and rubber. Further, metal and glass may also be employed.

Of these recording materials, when images are formed specifically on PET film, OPS film, OPP film, ONy film, or PVC film which are thermally shrinkable, the effects of the present invention are more pronounced. These substrates tend to curl and deform due to contraction during ink curing and heat generated during the curing reaction. In addition, it is difficult for the ink layer to keep up with contraction of the aforesaid substrate.

[0140]

The surface energy values of the aforementioned plastic films different from each other. It has been a problem that a dot diameter after ink-jetting varies depending on the recording materials. The preferred composition of the present invention includes OPP film and OPS film having a low surface energy and PET film having a relatively large surface energy. A wide variety of recording materials having a wettability index of 0.035 to 0.06 J/m² can be used to yield

a detailed image. Preferred recording materials for the present invention are those having a wettability index of 0.040 to 0.06 $\rm J/m^2$.

[0141]

In the present invention, form the viewpoint of the cost of recording materials such as packaging cost as well as production cost, print production efficiency, and compatibility with prints of various sizes, it is more advantageous to used long (web) recording materials.

[0142]

[EXAMPLES]

The present invention will now be detailed with reference to examples. However, the present invention is not limited thereto.

[0143]

<Preparation of Ink-jet Ink>

Magenta Pigment Dispersion was prepared using the formulation below.

[0144]

C.I. Pigment Red-184

15 weight parts

Polymer dispersing agent

2 weight parts

Aron Oxetane OXT-221 (manufactured

by Toa Gosei)

83 weight parts

Subsequently, the following blending was carried out. The resulting mixture was filtered employing a 0.8 μ membrane filter and dehydrated under vacuum while heated at 50 °C, whereby Magenta Inks 1 - 6 were prepared.

[0145]

(Magenta Ink 1)

Magenta Pigment Dispersion 17 weight parts

Multifunctional oxetane (Compound

Example 1) 80 weight parts

Celoxide 2021P (Daiseru UCB) 20 weight parts

SP-152 (photolytically acid

generating agent, manufactured

by Asahi Denka Co.) 5 weight parts

(Magenta Ink 2)

Magenta Pigment Dispersion 17 weight parts

Multifunctional oxetane (Compound

Example 4) 80 weight parts

Celoxide 2021P (Daiseru UCB) 20 weight parts

UVI-6990 (photolytically acid

generating agent, manufactured

by Dow Chemicals) 5 weight parts

(Magenta Ink 3)

Magenta Pigment Dispersion 17 weight parts

Multifunctional oxetane (Compound Example 5) 70 weight parts Celoxide 2021P (Daiseru UCB) 20 weight parts Celoxide 3000 (Daiseru UCB) 10 weight parts SP-152 (photolytically acid generating agent, manufactured by Asahi Denka Co.) 5 weight parts (Magenta Ink 4) Magenta Pigment Dispersion 17 weight parts Multifunctional oxetane (Compound Example 7) 70 weight parts Celoxide 2021P (Daiseru UCB) 20 weight parts Celoxide 3000 (Daiseru UCB) 10 weight parts UVI-6990 (photolytically acid generating agent, manufactured by Dow Chemicals) 5 weight parts (Magenta Ink 5) Magenta Pigment Dispersion 17 weight parts Multifunctional oxetane (Compound Example 2) 40 weight parts Aron Oxetane OXT-221 (manufactured by Toa Gosei) 30 weight parts

Celoxide 2021P (Daiseru UCB)

20 weight parts

SP-152 (photolytically acid

generating agent, manufactured

by Asahi Denka Co.)

5 weight parts

(Magenta Ink 6): Comparative Example

Magenta Pigment Dispersion

17 weight parts

Aron Oxetane OXT-221 (manufactured

by Toa Gosei)

40 weight parts

Aron Oxetane OXT-211 (manufactured

by Toa Gosei)

30 weight parts

Celoxide 2021P (Daiseru UCB)

30 weight parts

SP-152 (photolytically acid

generating agent, manufactured

by Asahi Denka Co.)

5 weight parts

Each of the inks prepared as above was ejected onto sheets of a corona treated PET (polyethylene terephthalate) film as a substrate, employing piezo type ink-jet nozzles (nozzle pitch of 360 dpi wherein dpi represents the number of dots per inch or per 2.54 mm) capable of forming a liquid droplet volume of 7 pl, while maintaining the nozzle section at 50 °C. Employed as a light source was a fluorescent tube having a main peak at 308 nm. Exposure was initiated 0.2 second after ink impingement under conditions of the illuminance on the substrate surface of 10 mW/cm² just under

the light source, and after 0.7 second, exposure was terminated (at an exposure energy of 5 mJ/cm²). The aforesaid test was carried out at a low humidity ambience (25 °C and 20 percent). Further, in order to evaluate ambience adaptability, Inks 1, 5, and 6 were evaluated in the same manner as above at a high humidity ambience (25 °C and 80 percent).

[0146]

Ink curability, close adhesion property to substrates, and image bleeding were evaluated.

<Ink Curability>

- A: No tackiness was noticed even though touched immediately after exposure
- B: Slight tackiness was noticed when touched after exposure, but after one minute, tackiness was not noticed
- C: Tackiness was noticed even one minute after exposure
 <Close Adhesion Property to Substrates>
- A: The image was not peeled off using a tape peeling procedure
- B: The image was partially peeled off using a tape peeling procedure
- C: The image was entirely peeled off using a tape peeling procedure

<Image Bleeding>

A: Almost no bleeding between adjacent dots was noticed

B: Slight bleeding between adjacent dots was noticed

C: Marked bleeding of dots was noticed

[0147]

(Table 1)

Ink	Ambience (humidity)	Ink Curability	Close Adhesion Property to Substrates	Image Bleeding
1	20%	A	A	A
1	80%	A	· A	A
2	20%	A	A	A
3	20%	A	A	A
4	20%	A	A	A
5	20%	A	A	A
5	80%	A	A	A.
6	20%	В	В	В
6	80%	С	С	С

[0148]

The same evaluation was carried out, except that the exposure was initiated 0.6 second after ink impingement and after 1.1 seconds, exposure was terminated.

[0149] (Table 2)

Ink	Ambience (humidity)	Ink Curability	Close Adhesion Property to Substrates	Image Bleeding
1	20%	A	A	A
1	80%	A	A	В
2	20%	A	А	A
3	20%	A	A	A
4	20%	A	A	A
5	20%	A	A	A
5	80%	А	А	A
6	20%	В	В	С
6	80%	С	С	С

[0150]

As can clearly be seen in Tables 1 and 2, ink-jet inks according to the preset invention exhibited excellent curability, as well as excellent close adhesion property to substrates, and minimal image bleeding, irrespective of low or high humidity ambiences. Further, it can be seen that even though the exposure initiating time was slightly delayed, the aforesaid inks tended to show minimal image bleeding.

[0151]

[EFFECTS OF THE INVENTION]

It is possible to prepare an ink-jet ink which exhibits excellent curability, layer strength, close adhesion property

to substrates, and high speed photocurability, independent of ambient humidity.

[NAME OF DOCUMENT]

ABSTRACT

[SUMMARY]

[PROBLEMS TO BE SOLVED]

An objective of the present invention is to provide a high speed actinic radiation curable resinous composition which exhibits excellent curability, strength of cured layers, and close adhesion property to substrate, and is independent of ambient humidity, as well as an ink-jet ink and an image forming method using the same.

[MEANS TO BE SOLVED]

An actinic radiation curable resinous composition comprising a multifunctional oxetane compound having at least two oxetane rings in which at least one oxetane ring is an oxetane compound residual group represented by General Formula (1):

General Formula (1)

$$R_4$$
 R_3
 R_5
 R_6
 R_5

wherein R_1 - F_6 each represents a hydrogen atom, or a univalent or divalent organic group, and R_3 and R_4 or R_5 and R_6 do not simultaneously represent a hydrogen atom.

[SELECTED DRAWINGS]

None